UREA GREASE COMPOSITION

Field of the Invention

The present invention relates to a urea grease composition.

Background of the Invention

Urea grease is known as heat-resistant grease because it generally has a higher dropping point and superior thermal stability than general-purpose lithium-soap grease containing lithium soap as a thickening agent.

In recent years, it has been discovered that urea grease has superior wear resistance and lubricating properties than greases in which various metal soap and inorganic materials have been used as thickening agents.

It is thought that the superior wear resistance is because urea grease can form both a urea film and an oxide film on lubricated sliding surfaces.

Urea grease has achieved rapid growth as grease which may be conveniently applied to typical grease-lubricated locations, including a wide variety of bearings for vehicle constant-velocity joints, ball joints, wheel bearings, alternators and cooling fans, ball screws and linear guides of machine tools, a wide variety of sliding areas of construction equipment, and bearings and gears in steel equipment and various other industrial mechanical facilities.

The usage of urea grease has been rising steadily in particular applications, such as various kinds of vehicle parts including CVJs (constant-velocity joints) where there is a strong demand for durability and reduced friction and wear in sliding areas in response to the trend of the present times toward miniaturisation, weight reduction and a hostile use environment, and in steel

equipment which requires highly heat-resistant, wear-resistant lubricating grease.

Although developments are being made year by year in the properties of urea grease, the latest urea grease still has some points to be improved upon, depending on the desired application.

For instance, domestic electric appliances and office automation equipment in particular are required to have appropriate sound characteristics, whilst it is becoming necessary for vehicle parts to have a low-noise characteristics, abrasion resistance and low friction characteristics which are indispensable thereto.

Taking a vacuum cleaner as a familiar example of the noises produced by domestic electric appliances and office automation equipment, noise reduction requirements are becoming increasingly severe because the bearings therein have come to revolve at a high speed of 30,000 to 40,000 rpm as the reduction in size and increase in suction in such equipment has progressed, thereby resulting in high wind noise and tumbling noise.

In addition, it is desirable to minimise noises produced by the bearings of video cameras, video tape recorders and electronic equipment as they act as error signals and adversely affect electronic components.

Therefore, it is very effective if a grease capable of ensuring low noise and high lubricity could be applied to those bearings, and so the development of a grease having improved properties is desired.

Furthermore, the smoothness of vehicles is also being improved year by year under circumstances where progression of energy savings and fuel economy is accelerated, and so quality levels required of individual parts making up vehicles is being raised year by year.

To the sliding areas of these parts, therefore, application of a grease capable ensuring low noise and

high lubricity is highly desirable, and it is required to develop a grease having improved properties.

Summary of the Invention

A urea grease composition is provided comprising a lubricating base oil and from 2 to 30 wt.% of a thickening agent, with respect to the total weight of the urea grease composition and wherein said thickening agent is selected from the group consisting of:

(1) a mixture of a compound (a) and a compound (b), containing compound (a) at 20 to 80 mol %, relative to the total amount of compound (a) and compound (b);

(2) a mixture formed by mixing with a compound (c) with a mixture (1) or

(3) a compound (c) alone,

wherein the compounds are represented by the general formulae

(a) $R_1NHCONHR_2NHCONHR_1$;

(b) $R_3NHCONHR_2NHCONHR_3$; and

(c) $R_1NHCONHR_2NHCONHR_3$,

and wherein R_2 is a diphenylmethane group, R_1 is a C6-10 saturated alkyl group and R_3 is a C14-40 saturated and/or unsaturated alkyl group wherein unsaturated alkyl groups constitute at least 20 mol % of the R_3 alkyl group.

Further, a method of lubricating a bearing is provided, comprising packing the bearing with such urea grease composition. Yet further, a method of lubricating a sliding surface of a machine in a relative motion is provided, comprising lubricating said sliding surface with such urea grease composition.

Detailed Description of the Invention

Examples of lubricated parts of vehicles include various kinds of bearings, such as cooling fan bearings of a radiator, compressor bearings of an air conditioner and alternator bearings, constant-velocity joints, universal joints of a propeller shaft, gears and bearings

of a steering unit, ball screws, sliding areas of rack guides, and ball joints.

Smooth lubrication with low noise and low friction are directly linked to energy savings, fuel economy and smoothness of vehicles, and greases showing excellent properties in those applications are very useful. Hence, more effective greases are required.

On the other hand, examples of parts to be lubricated in other industries, which are limited in direct low-noise requirements as compared with vehicles, domestic electric appliances and office automation equipment, include a wide variety of bearings of auto-assembly robots, ball screws and linear guides of machine tools, various sliding areas of construction equipment, and various bearings of steel facilities.

Although the direct low-noise requirements for greases is limited in such applications, the noise coming out of grease is ascribable not only to a physical noise caused by stirring and flow of grease but also to noises made at the interface between lubricated surfaces (noise caused by extraneous substances on the interface and noises caused by metal-to-metal contact arising from breakage of oil film).

As a matter of course, it can be said that a substandard grease inferior in lubricity and contaminated with extraneous substances is prone to cause breakage of oil film and abrasion at the interface and the generation of unacceptable noise. Accordingly, the sound characteristic thereof is not improved unless lubricity is enhanced. In other words, greases having favorable sound characteristics mean that the lubricity thereof is also improved.

The low-noise properties of greases are further explained by taking a bearing as an example. In general, the lubricating mechanism of a grease on a rolling-element bearing is such that the grease which has been

packed in the bearing is temporarily swung and scattered by revolution, and thereafter a trace amount of grease or oil is fed to a sliding area as churning and channeling are repeated, thereby lubricating the sliding area. Therein, a sound caused by vibrations occurring between a tumbling element of the bearing and a rolling surface appears as a bearing noise.

The working precision of the bearing and contamination of the grease with extraneous substances and particles of thickening agent in the grease are factors which cause bearing noise. The sound characteristics vary considerably with the form and the type of not only dirt and dust intruding into grease but also of the thickening agent incorporated in the grease. In addition, such substances tend to constitute an obstacle to smooth lubrication.

In general, in the case of a urea grease, urea compounds which have been obtained by reacting amine and isocyanate are used as thickening agents and these are dispersed in the oil and maintain the grease state.

Urea grease is generally superior to soap grease in abrasion resistance because the urea compound(s) used therein as a thickening agent are likely to adsorb to metal surfaces. However, many of the urea compounds obtained by the afore-mentioned reaction between amine and isocyanate are in a hard granular state, thereby impairing the sound characteristics and having an adverse effect on smooth lubrication.

JP-A-1-139696, JP-A-2-77494 and JP-A-6-17080 concern the acoustic properties of urea grease.

JP-A-1-139696 discloses a thickening agent containing a mixture of diurea compounds (a) and (b) represented by the following formulae (a) and (b), respectively:

(a) $R_1NHCONHR_2NHCONHR_3$

(b) $R_4NHCONHR_5NHCONHR_6$

wherein R_2 is a diphenylmethane group, R_1 and R_3 each represents a C8 linear or branched saturated alkyl group, R_5 represents a tolylene group or a bitolylene group, and R_4 and R_6 each represents an alkyl-substituted aromatic group or a halogen-substituted aromatic group.

JP-A-2-77494 discloses a thickening agent containing a mixture of diurea compounds (a) and (b) represented by the foregoing formulae (a) and (b) wherein, however, R_2 represents a bitolylene group, R_1 and R_3 each represent a C18 linear or branched saturated alkyl group or unsaturated alkyl group, R_5 represents a diphenylmethane group, and R_4 and R_6 represent C8 linear or branched saturated alkyl groups.

JP-A-6-17080 discloses a thickening agent containing a mixture of diurea compounds (a) and (b) represented by the foregoing formulae (a) and (b) wherein, however, R_2 represents a tolylene group, R_1 and R_3 represent C16-18 linear or branched saturated alkyl groups or unsaturated alkyl groups, R_5 represents a diphenylmethane group, and R_4 and R_6 represent C8 linear or branched saturated alkyl groups.

The following are other examples of literature on acoustic properties.

JP-A-3-28299 discloses a grease composition wherein the base oil containing an alkyldiphenyl ether oil as an essential component is mixed with a thickening agent which is a diurea compound represented by the foregoing formula (a) wherein, however, R_2 represents a C6-15 aromatic hydrocarbon group, and R_1 and R_3 represent C8-18 linear alkyl groups, provided that the proportion of C8 alkyl groups in the combination of R_1 and R_3 is from 60 to 100 mole %.

Page 8, Table 2 of JP-A-2-80493 discloses a composition for circular conical roller bearings which is

prepared by admixing urea grease with 0.5 to 5 % by weight of oxidation-modified polyolefin and/or acid-modified polyolefin, and further discloses in Table 2 the urea thickening agents prepared from C8 octylamine, C18 stearylamine (octadecylamine) and MDI (diphenylmethane-4,4'-diisocyanate) and demonstrates that these agents produce beneficial effects on machine stability, wet shear stability and pressure transferability.

JP-A-3-243696 discloses a diurea compound represented by the foregoing formula (a) wherein, however, R_2 is a 3,3'-dimethyl-4,4'-biphenylene group and R_1 and R_3 are mixtures of C8-18 alkyl groups with an oleyl group. The art disclosed in this document has defects that the consistency yield is so low that grease having a consistency of about 250 cannot be obtained without increasing the amount of the thickening agent and the degree of oil separation under high temperature conditions is great.

JP-A-58-185693 discloses a diurea grease improved by incorporating therein one or more of an additive selected from alkenylsuccinic acid imides, metal salts of alkylbenzenesulfonic acids, or metal salts of petroleum sulfonic acid. The document further discloses the use of diisocyanate and monoamines for the diurea grease, and recites aliphatic amines, such as stearylamine and oleylamine, and aromatic amines, such as cyclohexylamine, as examples of those monoamines. Said document indicates that the sound characteristics of said grease were favorable.

Further cases are cited below where production methods are examined in order to improve the sound characteristics of urea grease.

For instance, JP-A-2-4895 discloses a urea grease preparation method enabling improvement in sound characteristics, wherein an isocyanate and an amine are added to a base oil and reacted with each other at a

temperature of 60 to 120°C, and then the mixture of a urea compound produced and the base oil is subjected to dispersion treatment by use of a kneading apparatus and further heated up to 160 to 180°C at a temperature-rising speed of 0.5 to 2°C per minute.

JP-A-3-190996 discloses a method of preparing greases which are said to have good sound characteristics, wherein the isocyanate-dissolved or dispersed base oil and the amine-dissolved or dispersed base oil are mixed through collisions by pressurizing them in a reaction vessel to cause reaction with each other, or they are pressurized and introduced to an revolving impeller, thereby causing reaction with each other.

In addition, JP-A-3-231993 discloses a method of preparing low-noise urea grease, which includes the first step of heating the mixture constituted of 2 to 30 % by weight of a urea compound represented by the foregoing formula (a), wherein R_1 and R_3 are C8-18 saturated alkyl groups and R_2 is a tolylene group, a diphenylmethane group or a dimethylbiphenylene group, and 98 to 70 % by weight of a base oil up to 170 to 230°C to thoroughly dissolve the urea compound into the base oil, and the second step of cooling the solution obtained in the first step at a speed of at least 5°C per second.

As in the above documents, in many cases tolylenediisocyanate (TDI) or 3,3'-dimethyl-4,4'-biphenylenediisocyanate (TODI) have been used as starting materials for obtaining urea grease compositions having good sound characteristics.

With respect to the preparation methods thereof, the agglomeration of urea compounds is avoided by using kneading apparatus, performing the reaction in a high-pressure vessel, or dissolving two or more kinds of grease by heating and then mixing them.

As urea grease production rises and the demand for low noise greases grows, there is demand for a clean working environment for grease production and better sound characteristics in the final products.

Many users demand an inexpensive high-performance grease, and urea greases using high-cost TODI as a raw material and requiring a complicated production process will not be commercially competitive.

Furthermore, from a Health and Safety perspective, increase in grease production requires additional care with regard to the handling of TDI as a raw material and the installation of special equipment. As a result, it is required to consider reinforcing production facilities for improvement in sound characteristics and extending production process time.

There have now been found in the present invention specific urea grease compositions having a satisfactory consistency yield, with little oil separation at high temperature and with outstanding sound properties and lubricating properties. In addition, said urea grease compositions may be produced in conventional grease-making facilities without the need for specialised equipment such as high-pressure kettles or kneading machines in order to disperse the thickening agent.

The urea grease compositions of the present invention have good lubrication capabilities and can easily spread on and are strongly adsorbed to friction surfaces. In addition, the intervened thickening function of the urea compounds in said grease composition is not an obstacle therein as extraneous matter. Therefore, the urea grease composition of the present invention causes no noise, and, in addition, can enhance the strength of oil film by its viscoelasticity and can form more effective lubrication film on sliding surfaces under a synergy with additives. Thus, favorable grease lubrication can be attained.

Accordingly, there is provided a urea grease composition containing a lubricating base oil and from 2 to 30 wt.% of a thickening agent, with respect to the total weight of the urea grease composition and wherein said thickening agent is selected from:

(1) a mixture comprising a compound (a) and a compound (b), containing compound (a) at 20 to 80 mol%, relative to the total amount of compound (a) and compound (b);

(2) a mixture formed by mixing a compound (c) with a mixture (1); or

(3) a compound (c) alone,

wherein the compounds are represented by the general formulae

(a) $R_1NHCONHR_2NHCONHR_1$;

(b) $R_3NHCONHR_2NHCONHR_3$; and

(c) $R_1NHCONHR_2NHCONHR_3$,

and wherein R_2 is a diphenylmethane group, R_1 is a C6-10 saturated alkyl group and R_3 is a C14-20 saturated and/or unsaturated alkyl group, wherein unsaturated alkyl groups constitute at least 20 mol% of the R_3 alkyl group.

Preferably, unsaturated alkyl groups constitute at least 25 mol%, more preferably at least 30 mol% of the R_3 alkyl group.

In a preferred embodiment of the present invention R_1 is a saturated C8 alkyl group and/or R_3 is a C14-20 saturated and/or unsaturated alkyl group wherein unsaturated alkyl groups constituting at least 20 mol% of the R_3 alkyl group are oleyl groups.

In a preferred embodiment of the present invention there is provided a urea grease composition containing a lubricating base oil and from 2 to 30 wt.% of a thickening agent, with respect to the total weight of the urea grease

composition and wherein said thickening agent is selected from:

(1) a mixture comprising compound (a) and compound (b), containing compound (a) at 20 to 80 mol%, relative to the total amount of compound (a) and compound (b);

(2) a mixture formed by mixing a compound (c) with a mixture (1); or

(3) a compound (c) alone,

wherein the compounds are represented by the general formulae

(a) $R_1NHCONHR_2NHCONHR_1$;

(b) $R_3NHCONHR_2NHCONHR_3$; and

(c) $R_1NHCONHR_2NHCONHR_3$,

and wherein R_2 is a diphenylmethane group, R_1 is a C8 saturated alkyl group, R_3 is a C14-20 saturated and/or unsaturated alkyl group, with the alkyl groups being such that this constituent includes at least 20 mol% of an oleyl constituent.

In the present invention, a urea grease having outstanding characteristics and performance is obtained when a thickening agent as described above is incorporated into a lubricating base oil in an amount of from 2 to 30 wt%, preferably from 5 to 20 wt% with respect to the total weight of the urea grease composition. When the content of urea compounds as thickening agent is less than 2 wt%, the thickening effect is small and it is impossible to form a grease. On the other hand, when the content of urea compounds as thickening agent exceeds 30 wt%, the grease becomes too stiff and no lubricating effect is obtained.

When the proportion of the urea grease composition constituted by compound (a) in mixture (1) is less than 20 mol% or exceeds 80 mol%, relative to the total amount of compound (a) and compound (b), there is little effect of using the mixture and there is no improvement in noise performance or oil separation.

The lubricating base oil used in the urea grease composition of the present invention, may conveniently be one or more of a vegetable oil, a mineral oil, and/or a synthetic oil.

Base oils of mineral origin may be mineral oils, for example those produced by solvent refining or hydroprocessing.

Base oils of synthetic origin may typically be hydocarbon oils such as C_{10}-C_{50} hydrocarbon polymers, for example liquid polymers of alpha-olefins (poly(α-olefin)), ester type synthetic oils, silicone oils and/or ether type synthetic oils. They may also be a mixture of these oils.

Examples of mineral oils that may conveniently be used include those sold by member companies of the Royal Dutch/Shell Group under the designations "HVI", "MVIN", or "HMVIP".

Polyalphaolefins and base oils of the type manufactured by the hydroisomerisation of wax, such as those sold by member companies of the Royal Dutch/Shell Group under the designation "XHVI" (trade mark), may also be used.

In a preferred embodiment, the urea grease composition of the present invention further includes a zinc compound as an additive.

Specific examples of zinc compounds that may be conveniently employed in the urea grease composition of the present invention include zinc dithiocarbamates such as zinc diethyldithiocarbamate, zinc dipropyl-dithiocarbamate, zinc dibutyldithiocarbamate, zinc dipentyldithiocarbamate, zinc dihexyldithiocarbamate, zinc didecyldithiocarbamate, zinc diisobutyldithiocarbamate, zinc di(2-ethylhexyl)dithiocarbamate, zinc diamyldithio-carbamate, zinc dilauryldithiocarbamate, zinc distearyl-dithiocarbamate and zinc diphenyldithiocarbamate, etc., and zinc ditolyldithiocarbamate, zinc dixylyldithio-carbamate, zinc diethylphenyldithiocarbamate, zinc

dipropylphenyldithiocarbamate, zinc dibutylphenyldithiocarbamate, zinc dipenylphenyldithiocarbamate, zinc dihexylphenyldithiocarbamate, zinc dioctylphenyldithiocarbamate, zinc dinonylphenyldithiocarbamate, zinc didecylphenyldithiocarbamate, zinc didocecylphenyldithiocarbamate, zinc ditetradecylphenyldithiocarbamate and zinc dihexadecylphenyldithiocarbamate. Similarly, specific examples of zinc dithiophosphates include zinc diethyldithiophosphate, zinc dipropyldithiophosphate, zinc dibutyldithiophosphate, zinc dipentyldithiophosphate, zinc dihexyldithiophosphate, zinc didecyldithiophosphate, zinc diisobutyldithiophosphate, - zinc di(2-ethylhexyl)dithiophosphate, zinc diamyldithiophosphate, zinc dilauryldithiophosphate, zinc distearyldithiophosphate, zinc diphenyldithiophosphate, zinc ditolyldithiophosphate, zinc dixylyldithiophosphate, zinc diethylphenyldithiophosphate, zinc dipropylphenyldithiophosphate, zinc dibutylphenyldithiophosphate, zinc dipentylphenyldithiophosphate, zinc dihexylphenyldithiophosphate, zinc diheptylphenyldithiophosphate, zinc dioctylphenyldithiophosphate, zinc dinonylphenyldithiophosphate, zinc didecylphenyldithiophosphate, zinc didodecylphenyldithiophosphate, zinc ditetradecylphenyldithiophosphate and zinc dihexaphenyldithiophosphate. The metallic elements such as S or P in these organometallic zinc compounds react with iron in frictional surfaces to form extreme pressure films of iron phosphide or iron sulphide, etc.; and the additive itself breaks down and inter-reacts with other additives to form a protective film.

Furthermore, surprisingly, the urea grease compositions of the present invention exhibit outstanding lubricating properties due to synergistic effects of such S-P type additives with the urea thickening agents of the present invention, which have outstanding penetration into the interface and adsorption.

The urea grease composition of the present invention may advantageously include a molybdenum compound therein as an additive.

Specific examples of molybdenum compounds that may be conveniently employed in the urea grease composition of the present invention include molybdenum dithiocarbamates such as molybdenum diethyldithiocarbamate, molybdenum dipropyldithiocarbamate, molybdenum dibutyl-dithiocarbamate, molybdenum dipentyldithiocarbamate, molybdenum dihexyldithiocarbamate, molybdenum didecyl-dithiocarbamate, molybdenum diisobutyldithiocarbamate, molybdenum di(2-ethylhexyl)dithiocarbamate, molybdenum diamyldithiocarbamate, molybdenum dilauryldithiocarbamate, molybdenum distearyldithiocarbamate and molybdenum diphenyldithiocarbamate, etc., and molybdenum ditolyl-dithiocarbamate, molybdenum dixylyldithiocarbamate, molybdenum diethylphenyldithiocarbamate, molybdenum dipropylphenyldithiocarbamate, molybdenum dibutylphenyl-dithiocarbamate, molybdenum dipenylphenyldithiocarbamate, molybdenum dihexylphenyldithiocarbamate, molybdenum dioctylphenyldithiocarbamate, molybdenum dinonylphenyl-dithiocarbamate, molybdenum didecylphenyldithiocarbamate, molybdenum didodecylphenyldithiocarbamate, molybdenum ditetradecylphenyldithiocarbamate and molybdenum dihexadecylphenyldithiocarbamate, and molybdenum dithio-phosphates such as molybdenum dipentyldithiophosphate, -molybdenum dipropyl dithiophosphate, molybdenum dibutyl-dithiophosphate, molybdenum dipentyldithiophosphate, molybdenum dihexyldithiophosphate, molybdenum didecyldithiophosphate, molybdenum diisobutyldithio-phosphate, molybdenum di(2-ethylhexyl)dithiophosphate, molybdenum diamyldithiophosphate, molybdenum dilauryl-dithiophosphate, molybdenum distearyldithiophosphate, -molybdenum diphenyldithiophosphate, molybdenum ditolyl-dithiophosphate, molybdenum dixylyldithiophosphate, -molybdenum diethylphenyldithiophosphate, molybdenum

dipropylphenyldithiophosphate, molybdenum dibutylphenyl-dithiophosphate, molybdenum dipentylphenyldithiophosphate, molybdenum dihexylphenyldithiophosphate, molybdenum diheptylphenyldithiophosphate, molybdenum dioctylphenyl-dithiophosphate, molybdenum dinonylphenyldithiophosphate, molybdenum didecylphenyldithiophosphate, molybdenum didodecylphenyldithiophosphate, molybdenum ditetra-decylphenyldithiophosphate and molybdenum dihexaphenyl-dithiophosphate, and molybdenum compounds as described in JP 5-66435 B1, that is to say molybdenum complexes that are reaction products of a fatty oil, diethanolamine and a molybdenum source.

These afore-mentioned molybdenum compounds readily adsorb positively to the metal surfaces which constitute sliding surfaces, and are decomposed by the heat produced at the frictional surfaces to produce MoO_3 and MoS_2, and this MoS_2 component diffuses into the metal and has a mechanism of action which protects the frictional surfaces.

In addition, the urea grease compositions of the present invention exhibit outstanding lubricating properties due to synergistic effects of the chemical properties of these molybdenum compounds and physical and chemical properties such as adsorption and penetration of the urea thickening agents of the present invention.

Additives such as antioxidants, corrosion protecting agents and extreme pressure agents may be conveniently added to urea grease of the present invention in order to further improve the performance thereof.

For example, antioxidants including alkylphenol, hindered phenol, alkylamine, diphenylamine and triazine antioxidants; anticorrosion agents include calcium sulphonate, sodium sulphonate, barium sulphonate and amino derivatives or metal salts of carboxylic acids; and extreme pressure agents including sulphurized oils or fats, sulphurized olefins, phosphoric acid esters,

tricresyl phosphate, trialkyl thiophosphates and triphenyl phosphorothionates may be conveniently used.

Lubricants for bearing use may advantageously comprise the urea grease composition of the present invention.

Accordingly, the present invention further provides a method of lubricating a bearing comprising packing the bearing with the urea grease composition of the present invention.

In addition, lubricants for application to a sliding surface of a machine in a relative motion may advantageously comprise the urea grease composition of the present invention.

Accordingly, the present invention further provides a method of lubricating the sliding surface of a machine in a relative motion comprising lubricating said sliding surface with the urea grease composition of the present invention.

The present invention further provides the use of the urea grease composition of the present invention as a noise-reducing grease composition and, in particular, the use of said grease composition to reduce noise in bearing applications.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Examples 1-5

MDI (diphenylmethane-4,4'-diisocyanate) in the compounding proportions indicated in Table 1 and 60 parts by weight of base oil were introduced into a grease kettle and heated to approximately 50°C; and after dissolving the MDI, octylamine dispersed in 20 parts by weight of the base oil was slowly added with brisk stirring. After approximately 10 minutes, oleylamine dispersed in 20 parts

by weight of the base oil was added and stirring was continued.

The temperature of the contents of the grease kettle were raised by the reaction of the diisocyanate and the amine, and the reaction was completed by heating to 168°C and holding at this temperature for approximately 30 minutes, followed by cooling to room temperature and then treatment in a triple roll mill to obtain grease.

<u>Examples 6 and 7</u>

MDI in the compounding proportions indicated in Table 1 and 60 parts by weight of base oil were introduced into a grease kettle and heated to approximately 50°C, and after dissolving the MDI, a mixture of octylamine and oleylamine dissolved in 40 parts by weight of the base oil was slowly added to the solution and the mixture was stirred vigorously. The contents of the grease kettle were heated to 168ºC and held at this temperature for approximately 30 minutes to complete the reaction, and then cooled to room temperature and treated with a triple roll mill to obtain grease.

<u>Examples 8-10</u>

The compounding proportions are shown in Table 2. 50 parts by weight of the grease of Example 1 and 50 parts by weight of grease of Example 6 were mixed uniformly with a spatula to give the grease of Example 8.

50 parts by weight of the grease of Example 2 and 50 parts by weight of grease of Example 6 were mixed uniformly with a spatula to give the grease of Example 9.

50 parts by weight of the grease of Example 3 and 50 parts by weight of grease of Example 6 were mixed uniformly with a spatula to give the grease of Example 10.

<u>Examples 11-16</u>

MDI (diphenylmethane-4,4′-diisocyanate) in the compounding proportions indicated in Tables 3 and 4 and 60 parts by weight of base oil were introduced into a grease

kettle and heated to approximately 50°C, and after dissolving the MDI, 20 parts by weight of octylamine dissolved in the base oil was slowly added with brisk stirring. After approximately 10 minutes, the amines other than octylamine mixed in the composition shown in Table 3 with 20 parts by weight of base oil were added and stirring was continued.

The temperature of the contents of the grease kettle were raised by the reaction of the diisocyanate and the amine, and the reaction was completed by heating to 168°C and holding at this temperature for approximately 30 minutes, and then cooled to 80°C, followed by addition of the additives listed in Table 3 and then treated with a triple roll mill to obtain grease.

Comparative Examples 1-15

Diisocyanates in the compounding proportions indicated in Tables 5-7 and 60 parts by weight of base oil were put into a grease kettle and after dissolving the diisocyanates at the temperatures below, amines dispersed in 40 parts by weight of the base oil were slowly added with brisk stirring.

The contents of the grease kettle were heated to 168°C and held at this temperature for approximately 30 minutes to complete the reaction, and then cooled to room temperature and treated with a triple roll mill to obtain grease.

In Comparative Examples 13-15 the additives shown in Table 7 were added after cooling to room temperature, followed by treatment with the triple roll mill to give grease.

In Table 1 and Tables 3-7,

MDI is diphenylmethane-4,4'-diisocyanate; heating temperature approximately 50°C

TDI is 2,4/2,6 (80%/20%) trilene-4,4'-diisocyanate; heating temperature approximately 30°C

TODI is 3,3'-bitrilene-4,4'-diisocyanate; heating temperature approximately 75°C.

The viscosity at 100°C of the oils shown in the examples and comparative examples was 10.12 mm^2/s for mineral oil, 12.69 mm^2/s for alkyl diphenyl ether oil and 12.70 mm^2/s for poly(α-olefin) oil.

In the thickener mol% column in Tables 1 and 2,

(a) represents a compound $R_1NHCONHR_2NHCONHR_1$;

(b) represents a compound $R_3NHCONHR_2NHCONHR_3$; and

(c) represents a compound $R_1NHCONHR_2NHCONHR_3$,

wherein R_2 is a diphenylmethane group, R_1 is a C8 saturated alkyl group and R_3 is a C18 unsaturated alkyl group;

(1) indicates the diurea compound in Example 1,

(2) indicates the diurea compound in Example 2,

(3) indicates the diurea compound in Example 3, and

(6) indicates the diurea compound in Example 6.

The additives in Table 3, Table 4 and Table 7:

Additive A is a primary Zn-DTP (primary zinc dithiophosphate) with C4 and C5 alkyl groups,

Additive B is secondary Zn-DTP (secondary zinc dithiophosphate) with C3 and C6 alkyl groups,

Additive C is Zn-DTC (zinc dithiocarbamate) with C5 alkyl groups,

Additive D is Mo-DTC (molybdenum dithiocarbamate) with mainly C8 alkyl groups,

Additive E is a molybdenum complex compound as described in JP 5-66435 B1,

Additive F is Mo-DTP (molybdenum dithiophosphate) with predominantly C8 alkyl groups, and

Additive G is a slurry formed by compounding 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-*t*-butylamine)-1,3,5-triazine and octyldiphenylamine in a ratio 1:2 at a concentration of 50% with mineral oil.

Table 1

Example	1	2	3	4	5	6	7
MDI (g)	10.84	9.88	8.91	10.84	9.88	9.50	9.50
Octylamine (g)	9.15	6.10	3.05	9.15	6.10	4.91	4.91
Oleylamine (g)	4.01	8.02	12.04	4.01	8.02	9.59	9.59
Mineral oil (g)	176	176	176	-	-	176	-
Alkyl diphenyl ether (g)	-	-	-	176	176	-	-
Poly(α-olefin) (g)	-	-	-	-	-	-	176
Thickener (%)	12	12	12	12	12	12	12
Thickener (mol%)	(a)/(b) =75/25	(a)/(b) =50/50	(a)/(b) =25/75	(a)/(b) =75/25	(a)/(b) =50/50	(c) =100	(c) =100
Consistency (dmm)	245	241	241	232	245	225	247
Dropping point (℃)	>250	>250	>250	>250	>250	>250	>250
Oil separation (mass%)	0.6	1.1	2.4	0.4	0.8	0.4	0.7
Noise test after 120 s	5	12	12	10	8	7	7

Table 2

Example	8	9	10
Thickener (mol%)	(1) + (6) (a)/(b)/(c) =37.5/12.5/50	(2) + (6) (a)/(b)/(c) =25/25/50	(3) + (6) (a)/(b)/(c) =12.5/37.5/50
Thickener content (%)	12	12	12
Consistency (dmm)	232	235	233
Dropping point (°C)	>250	>250	>250
Oil separation (mass%)	0.5	0.4	0.4
Noise test after 120 s	5	7	7

Table 3

Example	11	12	13	14
MDI (g)	10.62	10.59	10.59	9.79
Octylamine (g)	8.52	8.52	8.52	6.04
Tetradecylamine (g)	0.15	0.12	0.12	0.20
Hexadecylamine (g)	0.36	0.33	0.33	1.67
C16 amine (C16 amine with one double bond) (g)	0.25	0.19	0.19	-
Stearylamine (g)	0.50	1.72	1.72	3.75
Oleylamine (g)	3.60	2.52	2.52	2.52
C20 amine (g)	-	0.02	0.02	0.03
Mineral oil (g)	126	176	50	50
Alkyl diphenyl ether (g)	-	-	-	76

Example	11	12	13	14
Poly(α-olefin) (g)	50	-	126	50
Thickener content (%)	12	12	12	12
Thickener (mol%)	(a)/(b) =70/30	(a)/(b) =70/30	(a)/(b) =70/30	(a)/(b) =50/50
R_3 unsaturated constituents (mol%)	78	55	55	30
Additive A (g)	2.0	2.0	-	2.0
B (g)	-	-	2.0	-
C (g)	-	-	-	-
D (g)	-	-	2.0	4.0
E (g)	4.0	2.0	-	-
F (g)	-	2.0	2.0	-
G (g)	2.0	2.0	2.0	2.0
Consistency (dmm)	255	243	253	248
Dropping point (°C)	>250	>250	>250	>250
Oil separation (mass%)	1.8	1.3	1.1	0.9
Noise test after 120 s	7	5	10	8
ASTMD2246 Shell 4 sphere impact resistance test (120rpm, 40kg, 75°C, 1h) mm	0.55	0.54	0.49	0.51
ASTMD3336 Bearing service life test (150°C, No. 6204,deep groove ball bearings)	>1000	>1000	-	>1000
Bowden friction test (room temp. sliding speed 10mm/s, surface pressure 1000 Mpa) coeff. of friction μ	0.128	0.130	0.127	0.129

Table 4

Example	15	16
MDI (g)	9.00	9.43
Octylamine (g)	3.65	4.85
Tetradecylamine (g)	0.28	0.32
Hexadecylamine (g)	2.32	2.73
C16 amine (C16 amine with 1 double bond) (g)	-	-
Stearylamine (g)	5.20	2.13
Oleylamine (g)	3.50	4.54
C20 amine (g)	0.05	-
Mineral oil (g)	176	176
Poly(α-olefin) (g)	-	-
Thickener content (%)	12	12
Thickener (mol%)	(a)/(b) =30/70	(c) =100
R_3 unsaturated constituents (mol%)	30	45
Additive A (g)	-	1.0
B (g)	-	-
C (g)	2.0	1.0
D (g)	-	-
E (g)	4.0	3.0
F (g)	-	1.0
G (g)	2.0	2.0
Consistency (dmm)	240	235
Dropping point (°C)	>250	>250
Oil separation (mass%)	2.2	1.5
Noise test after 120 s	4	8
ASTMD2246 Shell 4 sphere impact resistance test (120rpm, 40kg, 75°C, 1h) mm	0.52	0.48
ASTMD3336 Bearing service life test (150°C, No. 6204,deep groove ball bearings) h	-	>1000
Bowden friction test (room temp. sliding speed 10mm/s, surface pressure 1000 Mpa) coeff. of friction μ	0.126	0.129

Table 5

Comparative Example	1	2	3	4	5	6
MDI (g)	11.80	7.95	12.93	11.88	-	-
TODI (g)	-	-	-	-	12.13	12.27
TDI (g)	-	-	-	-	-	-
Octylamine (g)	12.20	-	-	-	11.87	-
Oleylamine (g)	-	16.05	-	-	-	11.73
p-Toluidine (g)	-	-	11.07	-	-	-
p-Chloroaniline (g)	-	-	-	12.12	-	-
Mineral oil (g)	176	176	176	176	176	176
Thickener content (%)	12	12	12	12	12	12
Consistency (dmm)	279	258	326	400	325	372
Dropping point (°C)	>250	185	>250	>250	>250	>250
Oil separation (mass%)	1.2	3.9	2.2	7.6	6.6	3.1
Noise test after 120 s	52	56	2,229	>10,000	151	191

Table 6

Comparative Example	7	8	9	10	11	12
MDI (g)	-	-	-	-	-	-
TODI (g)	13.25	12.21	-	-	-	-
TDI (g)	-	-	9.66	6.15	10.76	9.74
Octylamine (g)	-	-	14.34	-	-	-
Oleylamine (g)	-	-	-	17.85	-	-
p-Toluidine (g)	10.75	-	-	-	13.24	-
p-Chloroaniline (g)	-	11.79	-	-	-	14.26
Mineral oil (g)	176	176	176	176	176	176
Thickener content (%)	12	12	12	12	12	12
Consistency (dmm)	400	408	408	372	369	406
Dropping point (℃)	>250	>250	182	151	>250	>250
Oil separation (mass%)	4.6	3.5	20.5	80.5	3.4	5.3
Noise test after 120 s	461	>10,000	678	424	581	>10,000

Table 7

Comparative Example	13	14	15
MDI (g)	-	-	11.88
TODI (g)	12.21	-	-
TDI (g)	-	9.74	-
p-Chloroaniline (g)	11.79	14.26	12.12
Mineral oil (g)	176	176	50
Poly(α-olefin) (g)	-	-	126
Thickener content (%)	12	12	12
Additive A (g)	1.0	1.0	-
B (g)	-	-	1.0
C (g)	1.0	1.0	1.0
D (g)	-	-	3.0
E (g)	3.0	3.0	1.0
F (g)	1.0	1.0	-
G (g)	2.0	2.0	2.0
Consistency (dmm)	410	405	415
Dropping point (°C)	>250	>250	>250
Oil separation (mass%)	3.6	5.8	10.1
Noise test after 120 s	>10,000	>10,000	>10,000
ASTMD2246 Shell 4 sphere impact resistance test (120rpm, 40kg, 75°C, 1h) mm	-	-	-
ASTMD3336 Bearing service life test (150°C, No. 6204,deep groove ball bearings) h	680	380	520
Bowden friction test (room temp. sliding speed 10mm/s, surface pressure 1000 Mpa) coeff. of friction μ	Stick slip (discontinuous oil film)		

The properties of the examples and comparative examples in the tables were tested using the following methods.

Consistency : JIS K2220

Dropping point : JIS K2220

Oil separation : The JIS K2220 method was performed under the conditions of 150°C temperature for 24 hours.

Noise test : Bearing noise was measured for each grease using an NSK Noise Tester (available from NSK Ltd) as described in JP 53 2357 B1.

Bowden friction test: The coefficient of friction was measured using a device with the specifications below, which evaluated friction in a frictional surface between a reciprocating bed and a pin receiving a load vertical to a plate fitted to the bed, having a mechanism applying a load vertical to the bed.

1. Form: Reciprocal sliding friction tester
2. Test piece: Fixed side: steel sphere or rod
   Moving side: steel plate ca. 3 x 40 x 100 mm
3. Sliding speed: 0.05-20 mm/s
4. Sliding distance: 20-50 mm
5. Load: 0.1 kg to 10 kg
6. Temperature: Room temperature to 200°C
7. Drive method: Feed screw slide, lead 2 mm
8. Drive motor: AC servo motor 400 W

The results of these experiments demonstrate the following.

(1) It is possible to produce a urea grease composition according to the present invention, which has outstanding noise and lubricating properties, by using conventional facilities for grease production without the need for special equipment such as a kneading machine or a high-pressure kettle in order to bring about dispersion of the thickening agent.

(2) The urea grease composition of the present invention

gives an outstanding consistency yield, with a small quantity of thickener giving stiff grease; and

(3) The urea grease of the present invention has a high dropping point and does not show oil separation at high temperatures.